

Plutonium Magic

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A mysterious quality of enchantment: “For me the names of those men breathed the magic of the past” (Max Beerbohm).

adj. Of, relating to, or invoking the supernatural:

“stubborn unladen ghost/That breaks his magic chains at curfew time” (John Milton).

Possessing distinctive qualities that produce unaccountable or baffling effects.

Kmetko-Smith Phase Diagram and Magic

The Kmetko-Smith phase diagram (Figure 1) shows how the properties of plutonium metal seem to be “magic” when compared with those of their actinide neighbors in the periodic system. First, plutonium appears in a variety of complex crystal structures not found anywhere else in the periodic system. Second, there is an alarming minimum in the melting point that has significant implications for performance and manufacture. Other anomalous properties, such as the negative thermal expansion observed for the face-centered-cubic (fcc) δ -phase that is stable only at high temperature for the unalloyed metal, have also long been known for plutonium metal, whose behavior has often been construed as magic, in accordance with the last definition above. Finding the reasons for this appearance of magic properties was my goal as a research scientist at Los Alamos.

Zeta

The Kmetko-Smith diagram appeared in print at about the time I started at Los Alamos. My postilion was in the old CMB division (now split off into the Nuclear Materials Technology and Materials Science

and Technology Divisions), and my job was to determine the crystal structure of the ζ -phase (zeta phase) that appears in unalloyed plutonium with the application of modest pressures. I was assigned to the neutron scattering group that had just begun in what is now called the Los Alamos Neutron Science Center (LANSCE). I remained there more than twenty years, but never did succeed in my assigned task. However, I did learn

some other things that help explain the appearance of magic in plutonium (refer to Figure 2).

Pulsed Neutrons and Rietveld Analysis

I began my career in neutron scattering at a good time. I had had previous experience with x-ray diffraction studies of polycrystalline materials,

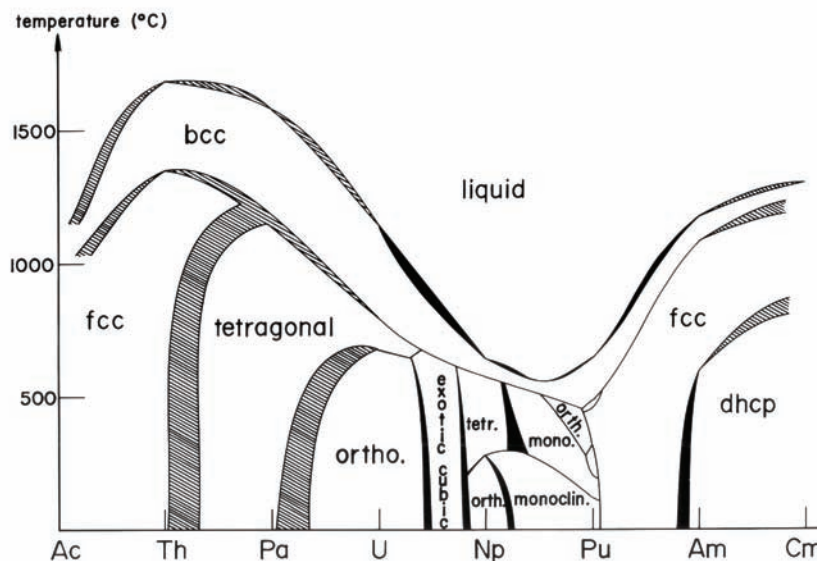


Figure 1. Kmetko-Smith Composite Phase Diagram

This diagram shows how the structures and melting point of the light actinides vary across the periodic table. The deep minimum in melting point is coincident with maximum structural complexity near plutonium's position.

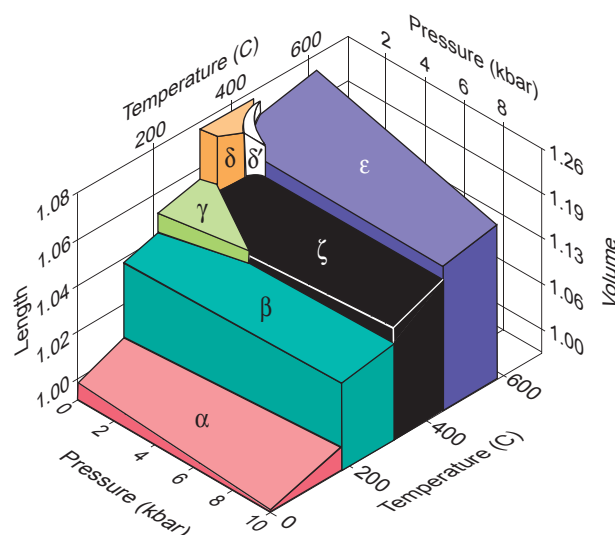


Figure 2. Pressure-Volume-Temperature Diagram for Unalloyed Plutonium Metal (after Morgan)

The ζ -phase is observed at moderately elevated temperatures and pressures, where it replaces the γ - and δ -phases. The crystal structure of the ζ -phase is so far unknown.

but there were three technical considerations that made the situation in Los Alamos quite favorable. First, in most circumstances, neutrons are more penetrating than x-rays, so that neutron diffraction data are more representative of the bulk of the specimen. Second, neutron scattering at LANSCE is based on pulsed-neutron diffraction, using neutrons derived from a proton accelerator. This means that the diffraction patterns can be taken at a fixed scattering angle and the resolution of the neutron diffraction is independent of crystallographic d-spacing. Third, a powerful analysis technique, “Rietveld” analysis, was just coming into play. Rietveld analysis provides rapid comparison of the experimentally obtained scattering data with data from a model structure, allowing models to be rapidly compared with reality. The method was soon adapted to the personal computer, which was new then, a development that made its application even more attractive.

Ammonium Fluoride and Uranium at IPNS

The facilities at LANSCE were not ready when I first arrived, so I spent several years traveling to the sister pulsed neutron source, the Intense Pulsed Neutron Source, or IPNS, at Argonne National Laboratory in Chicago. I participated in two experiments there that I construed as warm-ups for the ζ -plutonium problem. First, a group of us determined the crystal structure of a collapsed phase of the nitrogen-deuterium-fluoride compound ND_4F under pressures that were about the same as those required for ζ -plutonium—about 5 kilobars. This experiment was run at room temperature and below rather than at the high temperatures required for ζ -plutonium but was a good introduction to the high-pressure diffraction technique. In a second experiment, a group determined accurately the

crystal structure of β -uranium at high temperatures. This time, no pressure studies, but I learned that high temperatures were in some ways more challenging from the experimental point of view than the modest high pressures required for ζ -plutonium.

First Plutonium Experiment

I conducted my first plutonium experiment at LANSCE on a δ -phase plutonium-aluminum alloy ($\text{Pu}_{0.95}\text{Al}_{0.05}$). An important step was the design of a containment vessel that would keep all radiological contamination safely inside while making minimum contribution to the experimental signal. We managed to get six temperatures between 15 and 260 kelvins before running out of beam time. The results were astonishingly good. We got very precise values of the lattice constants and discovered, perhaps for the first time, that pulsed neutron diffraction combined with Rietveld analysis could give excellent results for the temperature dependence of the thermal motion of the atoms. Rietveld analysis can be used in measurements of atomic thermal motion because that motion causes the diffraction intensities to fall off drastically with d-spacing, and the rate of fall-off, which is a measure of the mean-square atomic thermal displacement, can be determined quite precisely when the Rietveld analysis is applied to diffraction data taken over a range of temperatures. The mean-square displacement is in turn a measure of the material’s elastic stiffness because the interatomic forces responsible for elasticity are in balance with the thermal agitation. The stiffness is expressed by the material’s so-called Debye-Waller characteristic temperature, so we had stumbled on to a good method for determining the elastic properties of plutonium by diffraction methods.

Plutonium Phases at IPNS and LANSCE

The plutonium research then split into two branches. At IPNS, we studied unalloyed plutonium at high temperatures, obtaining data on the α -, β -, γ -, δ -, δ' -, and ϵ -phases. We found that the furnaces available at IPNS did not have sufficiently good temperature control in the region below 600°C and constructed a special furnace with a very long time-constant and excellent temperature stability. A duplicate of this furnace was constructed for use at LANSCE. A separate experiment on unalloyed thorium was also conducted at IPNS. At LANSCE, we completed the study of δ -phase plutonium–5 atomic percent (at. %) aluminum and then concentrated on δ -phase plutonium-gallium alloys. Over a period of ten years, we studied three alloys containing 2, 4, and 6 at. % gallium.

Thermal Atomic Displacements and Melting

A particularly interesting feature of the early high-temperature data was the nonlinear behavior of the mean-square thermal atomic displacement with temperature. Instead of the linear behavior, shown approximately by thorium, we found that the displacement rises faster than linearly for the δ -phase plutonium alloys. Because our methods of measuring the displacement were not yet extensively tested, I was concerned that there was something wrong with the experiment, in particular, that the neutron absorption of plutonium—high even for the nominal plutonium-242 used in our studies—was introducing a bias into the results. After putting these worries to rest, I decided that the cause of the faster-than-linear increase of the atomic displacement with temperature must be the elastic stiffness of the alloy falling sharply with increasing temperature, up to the high-temperature limit

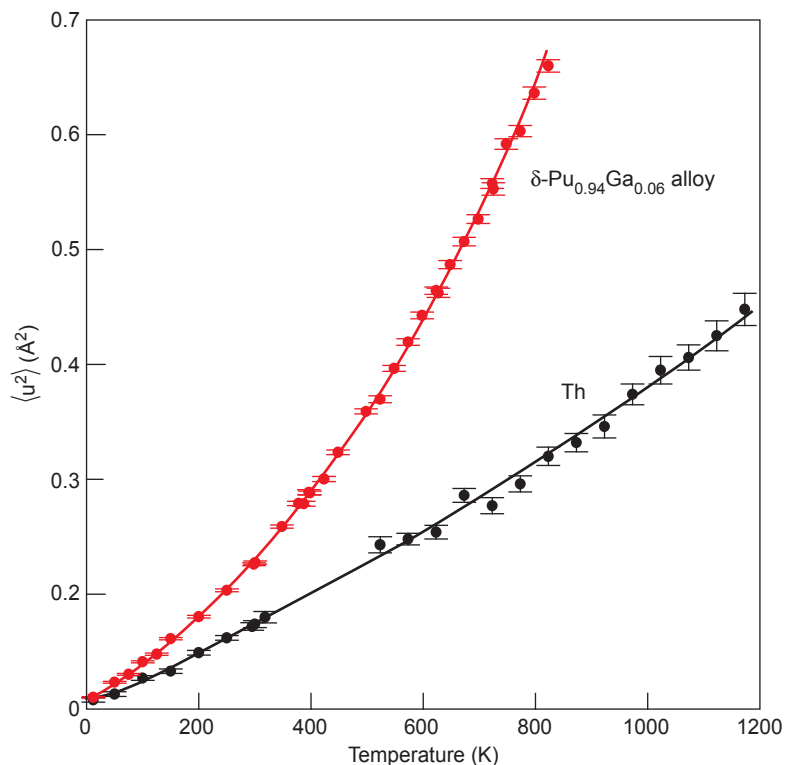


Figure 3. Mean-Square Thermal Atomic Displacement vs Temperature for δ -Phase plutonium and for thorium metal

The atomic displacement measures the increasing thermal agitation with temperature. The increase is approximately linear for most materials, but rises much more quickly for plutonium. This rapid rise explains the low melting point of plutonium, as melting is believed to occur when the displacement reaches about 10% of the interatomic distance.

of the δ -phase stability (see Figure 3).

Suddenly it struck me that this elastic softening behavior was the explanation for the low melting point of plutonium. The Lindemann rule, which goes back to 1910, states that a material melts when its mean-square thermal atomic displacement reaches about 10 percent of the interatomic distance. Although it is impossible to substantiate the Lindemann rule by theory, it is a sensible rule and gives fairly good results. Unfortunately, the rule failed for plutonium and predicted a melting point that was much too high. The problem was that the thermal displacements were estimated by the use of low-temperature elastic constants, and this procedure did not take the high-temperature elastic softening

into account. When the high-temperature softening was taken into account, the melting point predicted by the Lindemann rule was in good agreement with experiment. So I then knew that the low melting point of plutonium was “caused” by high-temperature elastic softening. It should be noted that plutonium does not melt from the fcc δ -phase but rather from the body-centered-cubic (bcc) ϵ -phase; because of the higher temperatures required to access the ϵ -phase, I deliberately chose to ignore this fact.

Zeta and Eta at IPNS

I hadn’t forgotten about the ζ -phase. I now had some experience with high-

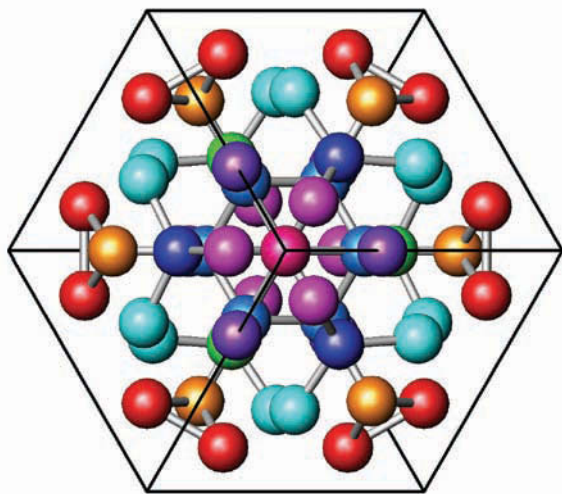
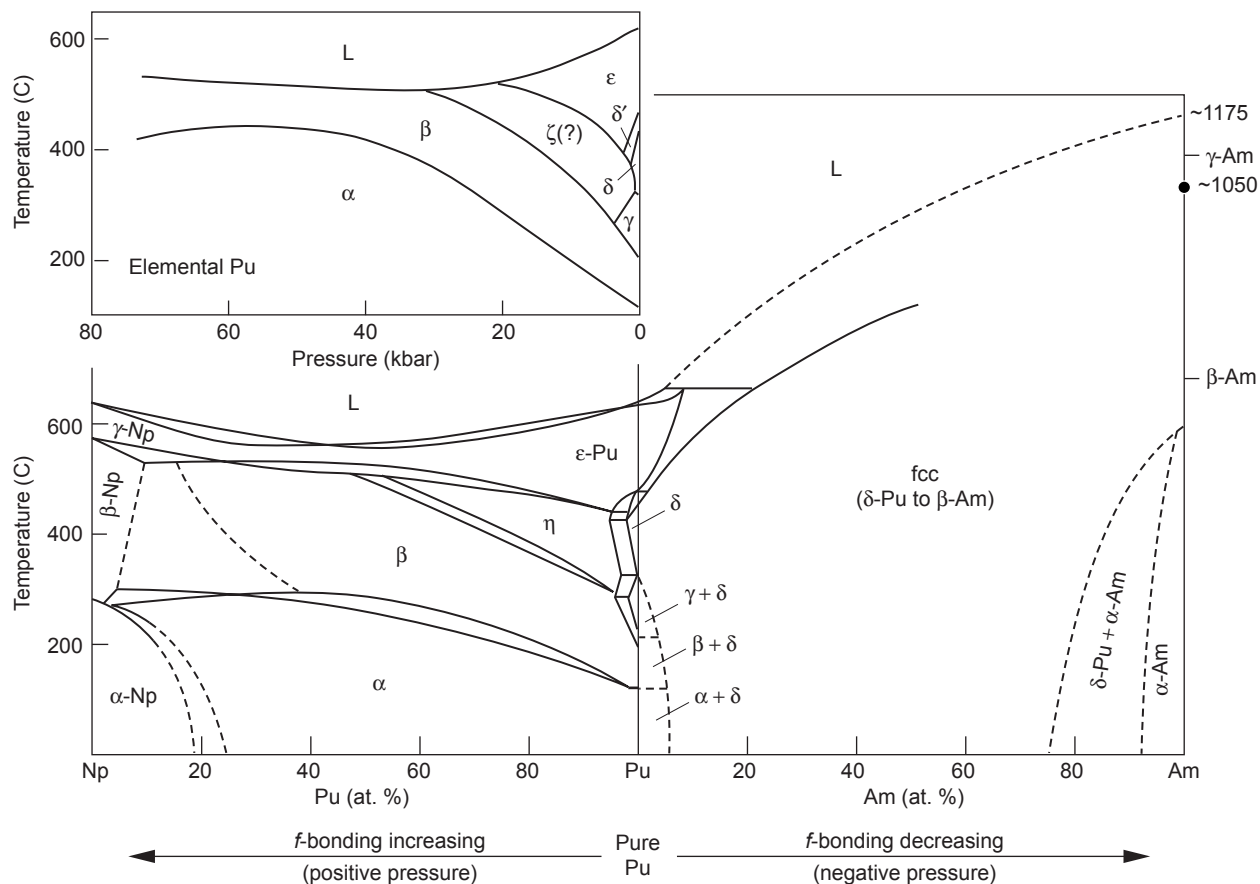


Figure 4. Comparative Phase Diagrams

Reed Elliott observed that the (reflected) pressure-temperature phase diagram of unalloyed plutonium looked just like the ordinary metallurgical phase diagram for plutonium-neptunium. He inferred from this observation that the structure of the ζ -phase for unalloyed plutonium is the same as that of the η -phase in the plutonium-neptunium system. (We are still trying to determine that structure from available data.)

Figure 5. Structure of the ζ -Phase in the Plutonium-Uranium System

This structure is not the same as the unknown structure of the ζ -phase in unalloyed plutonium, but is found in proximity to the η -phase in the plutonium-uranium system, which is believed to be similar. (The confusing nomenclature is unfortunately fixed by historical happenstance.) The ζ -structure shown has 10 crystallographically distinct plutonium atom types in its 58-atom unit cell and is the most complex structure found so far for a plutonium alloy.

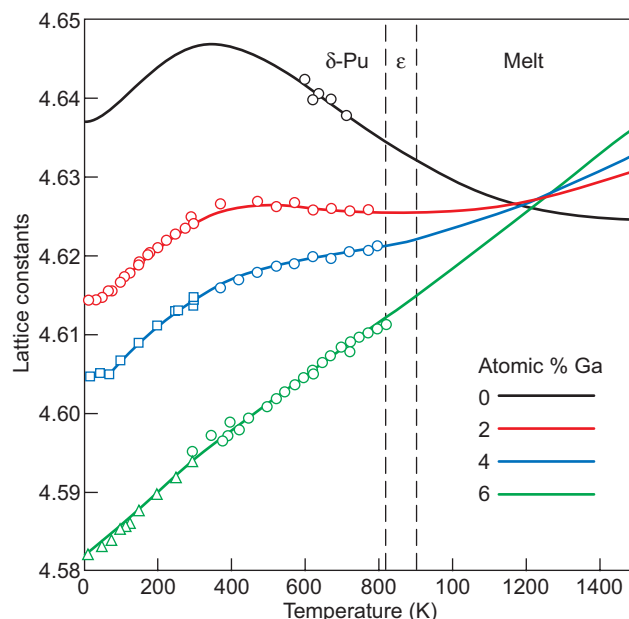


Figure 6. Lattice Constants of Unalloyed δ -Phase Plutonium and Several Plutonium-Gallium Alloys

These data taken by neutron diffraction at LANSCE and IPNS show the gradual transition from negative to positive thermal expansion at high temperatures that is characteristic of δ -plutonium. These data are in good agreement with the x-ray diffraction data published in 1960.

temperature experiments, but I could not find a practical way to do a safe experiment with both high temperatures and high pressures. I decided that the next best thing would be to determine the crystal structure of the η -phase (eta phase) in the plutonium-neptunium system. It had been convincingly demonstrated that alloying with neptunium was equivalent to the application of pressure, so that the determination of the plutonium-neptunium η -phase would also solve the ζ -phase of unalloyed plutonium (see Figure 4). It would certainly be a lot easier.

Experiments were conducted at IPNS on the η -phase of plutonium-neptunium and on the equivalent η -phase of plutonium-uranium, and data were successfully collected on these phases. As a bonus, data were also collected on the ζ -phase of plutonium-uranium (no relation to the ζ -phase of interest). I have so far (after more than ten years) been unable to solve the structure of the equivalent η -phases: They are just

too complicated. The plutonium-uranium ζ -phase was simpler, yet it was still very complicated because of its ten inequivalent actinide atom types in a large unit cell containing 58 actinide atoms (refer to Figure 5). This phase is even more complicated than the α - or β -phase of plutonium. One interesting idea that emerged from this study is that the α - and β -plutonium structures might usefully be construed as intermetallic compounds, just as the complex α -manganese phase, which coincidentally has 58 atoms per cell and 4 distinct atom types, is analogous to the intermetallic titanium-rhenium compound $\text{Ti}_5\text{Re}_{24}$.

Thermal Expansion and Invar

For an ordinary metal, the temperature dependence of the stiffness and the thermal expansion are intimately connected through a dimensionless ratio known as the Grüneisen

constant. The Grüneisen constant describes how the elastic stiffness, measured by the Debye temperature, varies with volume. This connection does not hold for δ -phase plutonium because the thermal expansion of unalloyed δ -phase is negative, and the temperature dependence of the volume varies strongly toward more normal positive values as plutonium is alloyed with aluminum or gallium, while the temperature dependence of the stiffness remains essentially constant. This astonishing and magical thermal-expansion behavior of the alloys was published in 1960 and was confirmed much later by the neutron diffraction measurements done at LANSCE (see Figure 6). The plutonium community has wondered for a long time about the magic of the thermal expansion of δ -plutonium.

Charles Edouard Guillaume won the 1920 Nobel Prize in physics for his development of iron alloys with zero and negative thermal expansion that revolutionized the art of metrology. His alloys are generically called “invar,” for invariant volume. A model put forward by Richard Weiss in 1963 explained the invar behavior by postulating the existence of two atomic states for iron, one with lower atomic volume and higher energy, and the other with higher atomic volume and lower energy. The model shows negative thermal expansion because a solid made from a collection of such atoms can access lower volumes at higher temperatures. I applied a similar model to δ -phase plutonium and found that it fit the thermal expansion perfectly. As shown in Figure 7, the energy difference turned out to be 1400 kelvins (or 120 milli-electron volts).

Magic and Invar

What is the connection between the invar thermal expansion and the temperature dependence of the stiffness?

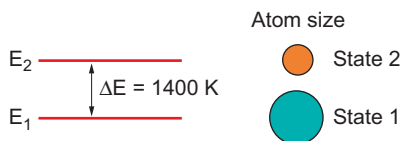


Figure 7. Schematic of the Two-Level Invar Model for δ -Plutonium The low-volume high-energy state is separated from the high-volume low-energy state by a small energy of 1400 K (or 120 meV).

To answer this question, I constructed a model free-energy function that included the energy of the invar levels. The invar energies have their own Grüneisen constant, which is allowed to vary with gallium content. So there are four model parameters, instead of the two for the normal Debye-Grüneisen solid. This model reproduces all the magic thermomechanical properties of δ -plutonium: the odd behaviors of the thermal expansion, the drastic elastic softening, and the consequent low melting point.

A glimmer of direct observation of the invar levels has been made with inelastic neutron scattering, but results are by no means certain yet. Finally, an identification has been made of the invar levels with the energies that appear in the theoretical dynamic mean-field calculations for δ -phase plutonium. It is perhaps not too early to hope that the origin of the magical properties of δ -plutonium will be found in the two-level invar model. Of course, it remains to be explained why, in terms of f-electron physics, these levels should be stable in the first place. Meanwhile, I will go back to the η -phase and hope that someone will eventually collect data on the magic ζ -phase.

All the pieces of the ζ -phase plutonium puzzle were on the table by 1965. Anyone could have applied Weiss's invar model to plutonium then, but it didn't happen. During my own time at Los Alamos, I was

unaware of the experimental elastic data until after I had completed the thermal displacement measurements at LANSCE. In retrospect, this is probably a good thing, because the effort required to conduct these measurements turned out to be strong motivation for eventually finding the source of plutonium magic in the two-state invar model. ■

Acknowledgment

I thought about listing the names of everyone who helped with this work, but the number of individuals who are owed both my personal thanks and those of the Laboratory must run into the hundreds. Therefore, I listed no one, but I am grateful to them all.

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